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PROGRESS REPORT OF THE SOLID STATE DIVISION FOR CALENDAR YEAR 1953

16 MARCH 1954

U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

PROGRESS REPORT OF THE SOLID STATE DIVISION FOR CALENDAR YEAR 1953

Prepared by:

Louis R. Maxwell

ABSTRACT: The annual progress report of the Solid State Division for the year 1953 will be devoted to accomplishments made in the field of basic research. Although considerable effort has been expended in certain applied research problems, it has been of a classified nature and in unrelated fields which makes it less suitable for review in the present report. The common goal of our efforts in our basic program is to gain a better understanding of the physics of solids, with practically our entire effort spent on magnetic investigations of certain non-metallic magnetic materials and studies carried out on semiconductors with emphasis placed on lead sulphide.

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It is now the policy of the Solid State Division to publish annually a brief report of each year's progress in the field of basic research. Such a policy serves two purposes: It delineates to other interested groups within the Naval Ordnance Laboratory the accomplishments made over the period concerned, and it constitutes an effective self-analysis carried out for the purpose of directing our efforts constantly into more fruitful and effective endeavors.

EDWARD L. WOODYARD
Captain, USN

H. J. Plumley

H. J. PLUMLEY
By direction

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PROGRESS REPORT OF THE SOLID STATE DIVISION FOR CALENDAR YEAR 1953

INTRODUCTION

1. During the year 1953, we initiated a new investigation into a class of substances known as the intermetallic compounds. This constitutes an increase in our effort in the field of semiconductors since the intermetallic compounds can be produced in such a way as to show the usual characteristics common to semiconductors which, therefore, affords a fruitful field for the study of the mechanisms basic to the electrical behavior of semiconductors. The project leader of the intermetallic group is Dr. R. M. Talley.

2. We have reduced our work in the field of electroluminescence, pointing toward the replacement of this effort by the investigations of the intermetallic compounds. Although there exist many unfinished and unsolved problems in the field of electroluminescence, it is felt that a more profitable use of our time can be spent on the intermetallic compounds, principally because of the simpler and known compositions of the materials used. We plan, however, to continue work on electroluminescence at a level sufficient to yield the necessary experiments for a Ph. D. dissertation. This will be one out of four such doctoral research projects now being undertaken in the Solid State Division. The recipients will receive their degrees either from the University of Maryland or Catholic University.

MAGNETISM IN SOLIDS

The Specific Heat Discontinuity in Antiferromagnets and Ferrites

3. An appreciable amount of the internal energy in a given magnetic material arises from the internal action between the magnetic ions present. The amount of this energy can be ascertained from the change in the total internal energy as the temperature of the material is raised through its Curie temperature. Howard and Smart have examined this phenomenon for both the ferrimagnetic and antiferromagnetic states using molecular field approximations. In particular, they found that the discontinuity in the specific heat at the Curie temperature is generally smaller for a ferrite than for a ferromagnetic or antiferromagnetic system having the same number of atoms. If non-magnetic atoms are substi-

FIG. I FLAME FUSION APPARATUS FOR GROWING SINGLE CRYSTALS OF REFRACTORY OXIDE MATERIALS

tuted for magnetic atoms located on the A sites then the specific heat discontinuity should usually decrease, whereas, if the non-magnetic atoms replace magnetic atoms on the B sites the discontinuity should usually pass through a maximum in a manner depending upon the nature of the internal forces. Certain experimental data on the specific heat of Ferroxcube III (maganese zinc ferrite) obtained by McGuire and Howard, are in rough agreement with this theory as regards the magnitude of the change in specific heat at the Curie temperature.

Sublattice Behavior for Non-Magnetic Trivalent Substitutions in Nickel Ferrite

Plan and Purpose

4. Important information concerning the ferrites can be gained through a study of the relationship between the magnetic properties and the number and type of trivalent magnetic ions present. A stable ferrite such as nickel ferrite was selected and a program undertaken whereby the trivalent iron ions were replaced by various trivalent non-magnetic ions. Trivalent aluminum and trivalent gallium have been used thus far for this purpose. A photograph of the equipment built for the preparation of single crystals of materials to be used in the study of this substitution series is given in Figure 1.

5. The Neel theory of ferrimagnetism is based upon the concept of the existence of two magnetic sublattices within the ferrite material. By introducing non-magnetic trivalent ions into the nickel ferrite we may vary the number of magnetic ions in the two sublattices. The way in which the magnetic ions will distribute themselves is not foreseen apriori, although there are certain indications as to the expected ionic distribution based on previous work on both magnetic and non-magnetic spinels. Independent, but related, experimental and theoretical investigations have been carried out on the systems mentioned above. New insight into the nature of ferrite materials is described below.

DC Magnetization

6. It was found by Maxwell and Pickart that for the nickel ferrite aluminate system, the saturation magnetization extrapolated to absolute zero, decreased as Al^{+++} replaced Fe^{+++}, approaching zero at a value of $t = 0.7$. At this point the magnetization of the two sublattices were equal in magnitude but opposite in direction. When additional aluminum

replaces the iron the saturation magnetization increases in the opposite direction and then returns toward zero at the end point, which is the nickel aluminate.

7. When Ga^{+++} replaces Fe^{+++}, the behavior is considerably different. No change in direction of the saturation magnetization exists at about $t = 0.70$ but rather a maximum occurs at this point.

8. The remarkably different behavior found between the Al and Ga substitutions can be understood in terms of the way in which the non-magnetic ions replace Fe^{+++}. The decrease in magnetization that results in the compensation point is caused by the Al^{+++} going preferentially to the B sites whose magnetization dominates over those ions on the A sites. When Ga is substituted, however, it prefers to replace the trivalent ions in the A sites which results in an increase of the resultant magnetization of the material.

9. Thermomagnetic data obtained from the nickel ferrite aluminates and nickel ferrite gallates showed curves whose general form was predicted by the Néel theory and in the case of the former, they were of such a nature that one could conclude, for certain values of t, that the B-B interactions are negative.

Magnetic Resonance Measurements

10. Experiments were conducted by McGuire on the magnetic resonance absorption of the nickel ferrite aluminate series at microwave frequencies. Through such investigations, it is possible to determine the g-values as a function of the distribution of the magnetic ions on the two sublattices. Figure 2 shows a photograph of the nuclear resonance equipment used to determine accurately the static magnetic field in which the electronic magnetic resonance takes place. In particular, it was of interest to see what sort of behavior occurs near the crossover or compensation point described above for the nickel ferrite aluminates. McGuire's results show that the g-values, plotted as a function of the amount of aluminum present, take on a shape somewhat similar to the well-known dispersion curves observed in optical phenomena. Other results which are more difficult to understand were observed, such as the appearance of two resonance absorption peaks under certain conditions and the formation of highly unsymmetrical absorption curves when plotted with respect to the applied magnetic field.

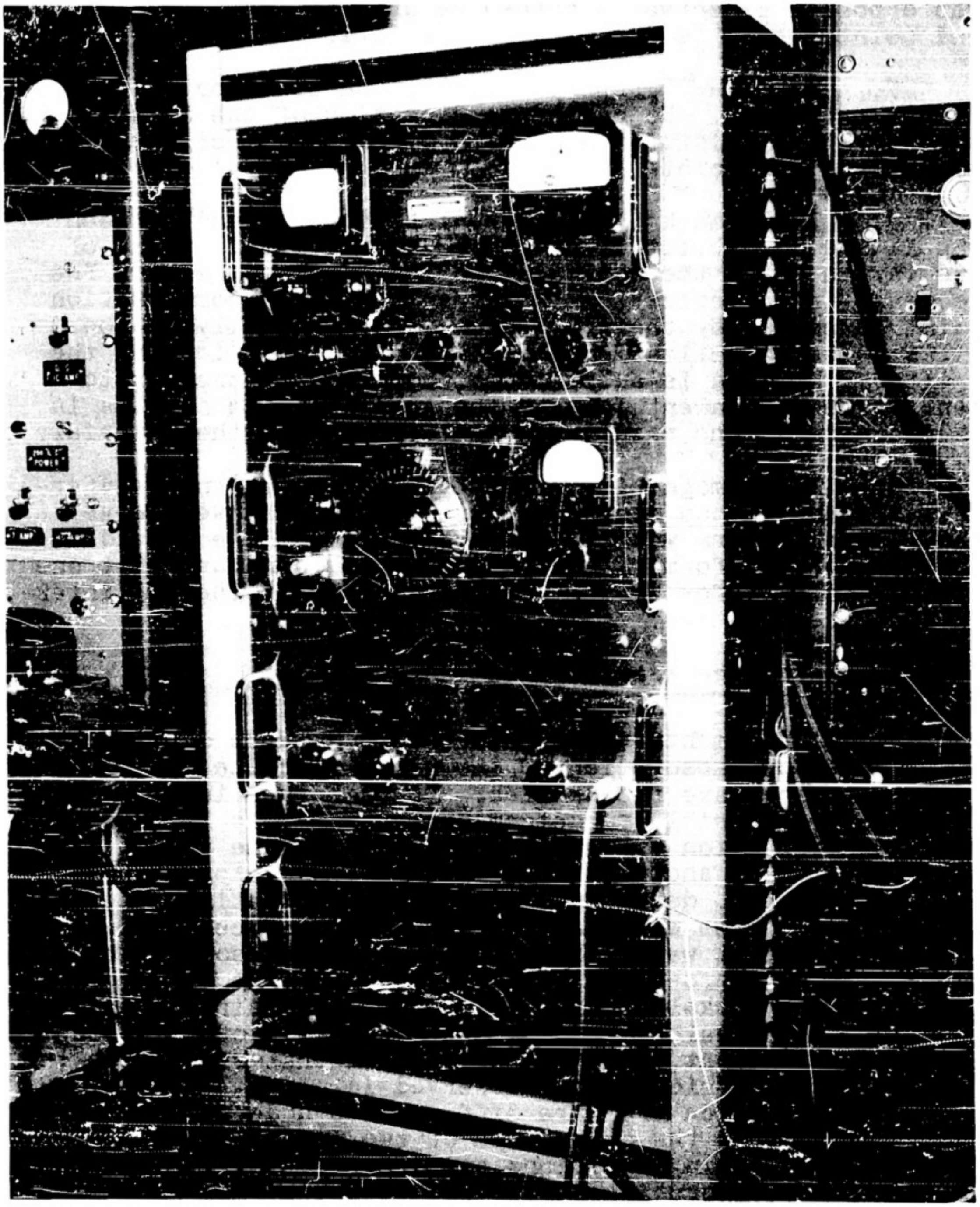

FIG. 2 VARIAN MAGNETIC FIELD METER

Theory of Sublattice Effects in Magnetic Resonance

11. Previously, the theory of ferromagnetic resonance had been used to interpret electronic magnetic resonance in ferrimagnetic systems. It was soon realized, however, that a more detailed analysis was necessary. Wangsness has examined this problem in detail, first on the basis of the existence of magnetic ions on two sublattices; and then with respect to the grouping of the atoms into four sublattices - a situation existing in certain mixed ferrites. Out of this study he obtained an effective g-value as follows:

$$g_{eff} = \frac{g_A S_A + g_B S_B - g_C S_C - g_D S_D}{S_A + S_B - S_C - S_D} \qquad (1)$$

where S_i is the spin angular momentum of the i^{th} sublattice.

12. We see from Equation (1) that the effective g-value depends upon the ratio of the algebraic sum of the magnetizations to that of the angular momenta. A test of this theory is found in the microwave resonance work of McGuire on the nickel ferrite aluminate system mentioned above. The resonance work showed that the g-value approached zero at the point where the net magnetization approached zero as predicted by Equation (1). Other features of the experimental determination of the g-values were found to be in general agreement with the theory as outlined by Equation (1).

13. Further clarification, however, was needed to ascertain the relationship between the theories of ferromagnetic and ferrimagnetic resonance absorption - the latter being based, for simplicity, upon a two-lattice model. Wangsness found that under the usual conditions that exist within a crystal - namely, that the product of the molecular field coefficient and the net magnetization is larger than both the applied and anisotropy fields - that the resonance condition for a ferrimagnetic state is identical to that for the ferromagnetic state; this is true provided one utilizes the concept of an effective g-factor. There are two rather obvious extensions of this theory, one in which the net magnetization approaches zero for a finite net angular momentum, and the other when the angular momentum approaches zero with a finite net magnetization. In the former instance, one obtains a resonance condition independent of the applied field and involving only the anisotropy field, while for the latter case, we approach very large but finite effective g-values.

ELECTRICAL BEHAVIOR OF SEMICONDUCTORS

Lead Sulfide

14. A basic property of a semiconductor is the existence of a forbidden energy gap. Photoconductivity and other semiconductor phenomena depend critically upon the energy difference of this gap (ΔE). For germanium and silicon, which are known as elementary semiconductors, the value of ΔE has been satisfactorily established. For the binary compound lead sulfide, there existed considerable uncertainty as to the value of ΔE. Some of the reported values were very difficult to reconcile with experiments on photoconductivity and infrared absorption for this material.

15. ΔE can be determined from measurements of the Hall effect or the electrical resistivity as a function of the temperature of the material. Scanlon believed that the question concerning the published values of ΔE for PbS were due to an appreciable change in the composition of the material that occurred during the measurements. He, therefore, performed a series of carefully controlled experiments which yielded true values of ΔE and furthermore demonstrated clearly that the earlier values were actually due to changes in composition of the material, which occurred at the temperatures used by other investigators.

16. A photograph of the set-up for growing single crystals of PbS is shown in Figure 3.

17. The value of ΔE obtained from single crystals of PbS was found to be 0.37 ± .01 e.v. which is in satisfactory agreement with optical data. We now have a clearer understanding of the behavior of lead sulfide with respect to its electrical conductivity, photoconductivity and Hall effect properties.

ELECTROLUMINESCENCE

18. When a phosphor is excited by an external light source the resulting intensity of luminescence can be affected by an applied alternating electric field. Nudelman has shown that the emitted light intensity is modulated in an unusual fashion. When the electric field is first applied there exists a momentary increase in intensity that dies off to a minimum lower than the equilibrium intensity followed by a subsequent slow increase to a new equilibrium value. In addition, there exists a periodic intensity fluctuation described as a "ripple" having a frequency twice that of the field

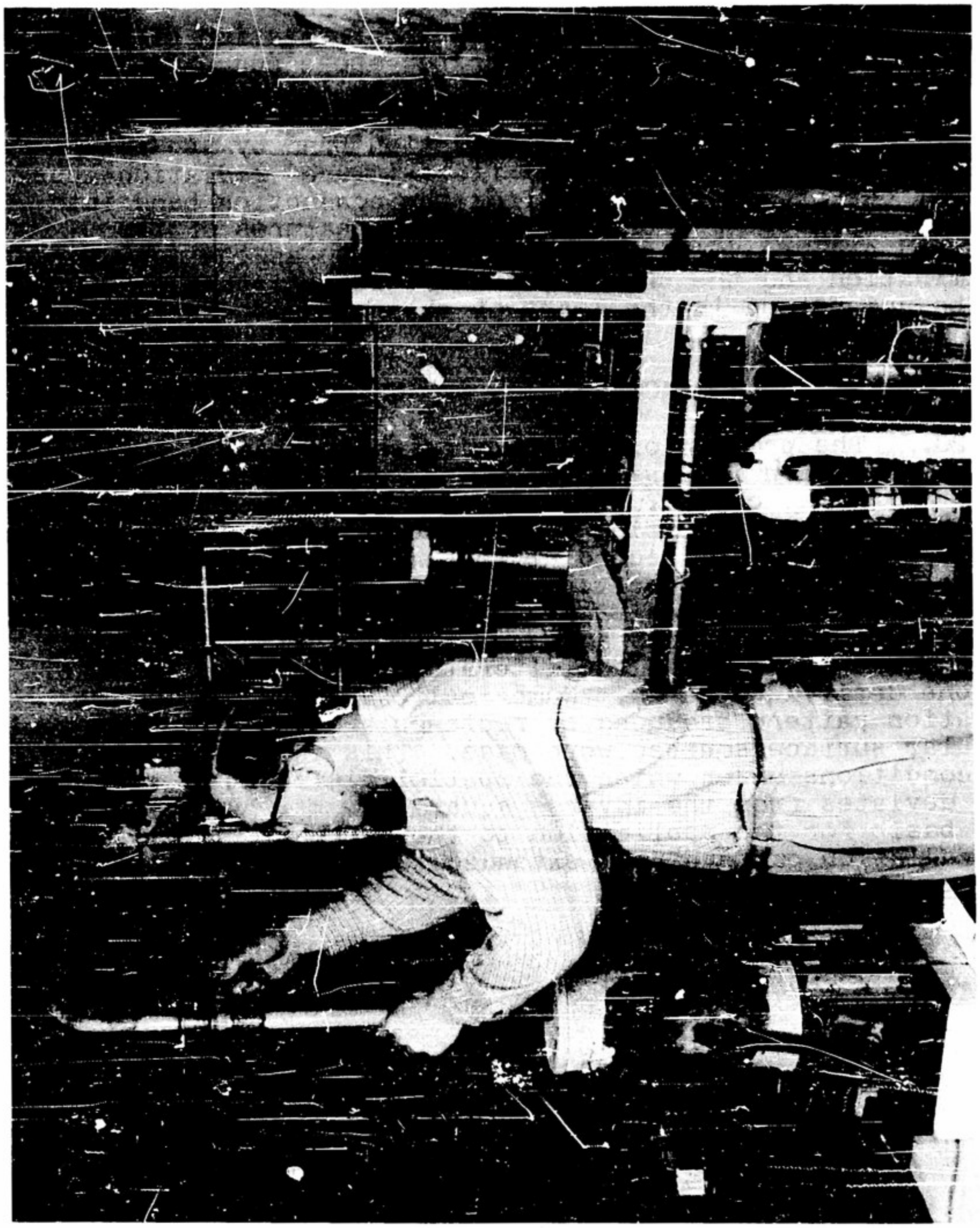

FIG. 3 PREPARING PbS CRYSTALS

frequency. Upon removal of the electric field another momentary increase of the light intensity occurs which then decreases to the original equilibrium value.

19. Matossi investigated the interpretation of the electroluminescent behavior described above and extended an earlier theory of Randall and Wilkins by introducing: (1) the possibility of liberating electrons existing in electron traps below but close to the conduction band by the action of the electric field, and (2) field-induced radiation-less transitions of the electrons from the conduction band into surface luminescence centers. Certain features of the observed electroluminescence effects, such as the momentary illumination and the subsequent decrease in intensity can now be understood in the light of these new concepts.

RADIATION CHARACTERISTICS OF SURFACE SOURCES

20. The problem of determining the spatial distribution of the radiation intensity emitted by surfaces having the form of a rectangle, circle, and semicircle, has been solved by Mahan under the assumption that these sources radiate uniformly over their extent according to Lambert's Cosine Law. A general equation was derived giving the total flux incident upon an elementary receiving area, at any point in space, whose surface normal has any arbitrary direction. Previous expressions reported in the literature are special cases of the one derived by Mahan. Numerical calculations for the radiation pattern produced by rectangular, circular, and semicircular surface sources were made. This information gives the conditions under which the spatial distribution of intensity deviates from the inverse square law. It will also serve as a basis for the application to the problem of determining the radiation pattern from extended surfaces and ones having more complex shape.

6. "On Noise in P-N Junction Rectifiers, I Theory" by Richard L. Petritz, American Physical Society Meeting, Durham, North Carolina, 26-28 March 1953

7. "On Noise in P-N Junction Rectifiers, II Experiments" by Frances L. Lummis and Richard L. Petritz, American Physical Society Meeting, Durham, North Carolina, 26-28 March 1953

8. "Theromagnetic Investigations of Nickel Ferrite-Aluminates" by Louis R. Maxwell, R. W. Hall, Stanley J. Pickart, American Physical Society Meeting, Durham, North Carolina, 26-28 March 1953

9. "Magnetic Resonance Absorption in Nickel-Ferrite-Aluminates" by Thomas R. McGuire, American Physical Society Meeting, Durham, North Carolina, 26-28 March 1953

10. "g-values of the Nickel-Ferrite-Aluminates" by Roald K. Wangsness, American Physical Society Meeting, Durham, North Carolina, 26-28 March 1953

11. "The Properties of Semiconductors" by Wayne W. Scanlon, American Association of Physics Teachers, George Washington University, Washington, D. C., 11 April 1953

12. "Magnetic Anisotropy in the Ferrites" by Henry Shenker, Physics Colloquium, University of Maryland, College Park, Maryland, 14 April 1953

13. "Trivalent Substitutions in the Ferrites" by Louis R. Maxwell, American Physical Society Meeting, Washington, D. C., 30 April 1953

14. "Interpretation of Some Electroluminescent Effects" by Frank Matossi, American Physical Society Meeting, Rochester, New York, 18-20 June 1953

15. "Antiferromagnetism" by J. Samuel Smart, Solid State Group, Naval Research Laboratory, Washington, D. C., 22 June 1953

16. "Electronic Magnetic Resonance and Its Application to Solid Solutions" by Louis R. Maxwell, Gordon Research Conference on Catalysis, New London, New Hampshire, 22 June 1953

17. "Static Magnetic Susceptibility Measurements" by Thomas R. McGuire, Microwave Ferromagnetics Seminar, Applied Physics Laboratory, Johns Hopkins University, Silver

Spring, Maryland, 7 October 1953

18. "Radiation Characteristics of Circular, Semicircular, and Rectangular Surface Sources" by A. I. Mahan, Optical Society of America Meeting, Rochester, New York, 15-17 October 1953

19. "Random Processes and Noise in Semiconductors" by R. L. Petritz, Washington Philosophical Society Meeting, Washington, D. C., 23 October 1953

20. "Magnetism in the Ferrites" by T. R. McGuire, National Bureau of Standards Low Temperature Physics Seminar, Washington, D. C., 27 October 1953

21. "Magnetic Resonance in Ferrimagnetics" by Roald K. Wangsness, Microwave Ferromagnetics Seminar, Applied Physics Laboratory, Johns Hopkins University, Silver Spring, Maryland, 28 October 1953

22. "Magnetic Structure Transitions" by J. Samuel Smart, Microwave Ferromagnetics Seminar, Applied Physics Laboratory, Johns Hopkins University, Silver Spring, Maryland, 18 November 1953

23. "Magnetism in the Ferrites" by Thomas R. McGuire, Physics Seminar, University of Maryland, College Park, Maryland, 24 November 1953

24. "Electroluminescence with Non-Sinusoidal Electric Fields" by Sol Nudelman and Frank Matossi, American Physical Society Meeting, Chicago, Illinois, 27 November 1953

25. "Theory of Noise in Photoconductive Cells" by Richard L. Petritz, Chicago Midway Laboratories, Chicago, Ill. 30 November 1953

26. "Theory of Noise in Photoconductive Cells" by Richard L. Petritz, Physics Department Colloquium, Northwestern University, Evanston, Illinois, 1 December 1953

In Foreign Countries

27. "Vibrational Emission Spectra in Glow Discharges" by Frank Matossi, University of Cologne, Cologne, Germany, September 1953

28. "Interpretation of Some Electroluminescent Effects" by Frank Matossi, Siemens Laboratories, Erlangen, Germany, September 1953.

29. "Group Theory of Molecular Vibrations" by Frank Matossi, University of Munich, Munich, Germany, September 1953

30. "Some Electroluminescence Effects and Their Interpretation" by Frank Matossi, Swiss Physical Society, Lugano, Switzerland, 5 September 1953

31. "Some Electroluminescence Effects and Their Interpretation" by Frank Matossi, German Physical Society, Innsbruck, Austria, 20 September 1953

32. "Antiferromagnetism" by J. Samuel Smart, Solid State Group, Philips Research Laboratories, Eindhoven, Netherlands, 14 October 1953

33. "Magnetic Resonance in Ferrimagnetics" by Roald K. Wangsness, Research Institute for Electrical Communications, Tohoku University, Sendai, Japan, 17 November 1953